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A method of forming polymer films

This invention relates to a method of forming a layer of polymer on a substrate.

It is well known in the art to use fluorinated, particularly perfluorinated, materials as coatings for lubrication or for passivation. Fluorinated materials are noted for possession of low coefficient of friction, low surface energy and a high degree of chemical inertness. It remains, however, a difficult problem to adhere a perfluorinated material to a substrate. Perfluorinated long chain acids and salts are rigid and have a tendency to crystallize. They also have relatively high viscosity, high vapour pressure and low cohesive energy. The combination of these properties makes it very difficult to build up a stable monolayer assembly of such a material on a substrate.

The prior art shows that multi-layer or monomolecular layers of vinyl stearate can be polymerized by a solid state reaction. See Peterman et al. J. Colloid and Interface Sci., *47*, 705 (1974), and A. Cemel et al. J. Polym. Sci., A—1, 2061 (1972).

According to the invention there is provided a method of forming a layer of polymer on a substrate surface comprising depositing on the substrate surface a monomolecular layer of a monomer, characterised in that the monomer has the formula

$$(CF_3—(CF_2)_n—(CH)_m—X—COO)_2\ M$$

or

$$(CF_3—(CF_2)_n—(CH_2)_m—X—(CH_2)_L—COO)_2\ M$$

wherein n is 6 to 20, each of m and L is 6 to 10, x is —CH=CH— or —C≡C—, and M is a divalent cation, and polymerizing said layer.

Preferably the polymerization is carried out by exposing the monomolecular layer to ultraviolet or gamma radiation.

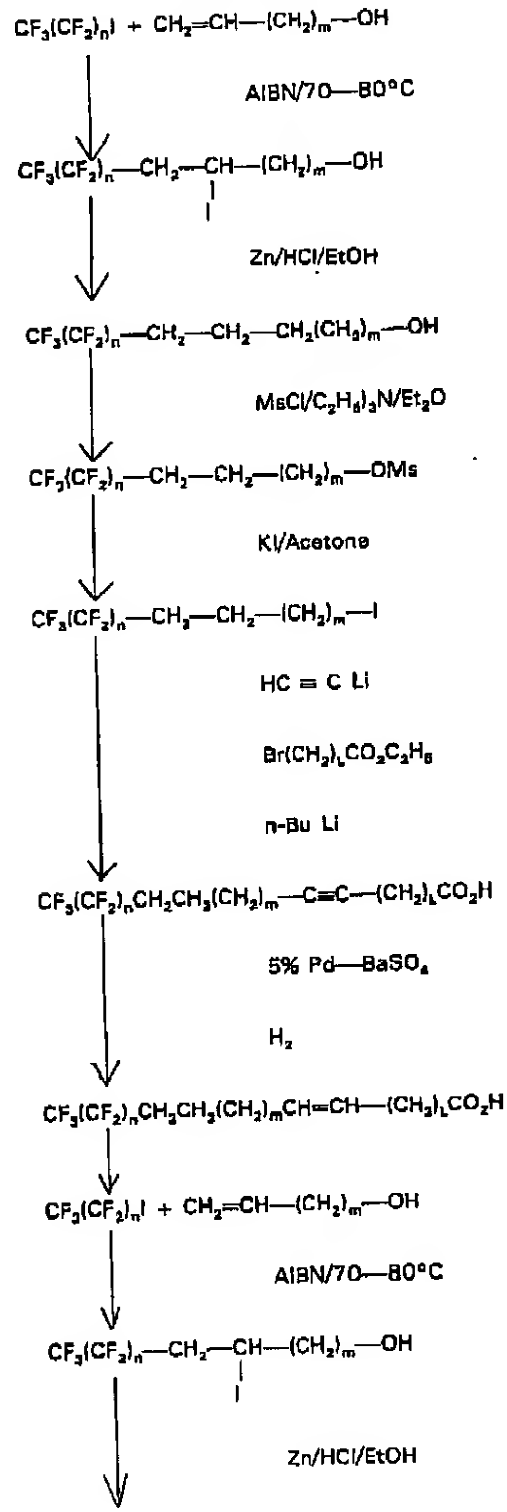
The particular solid substrates for the use of the present invention are hydrophilic surfaces like an oxidized metal, semi-conductor or dielectric. As particularly important examples, there may be mentioned silicon dioxide, aluminum oxide, fused silica and glass. The salt group enhanced the attachment of the monolayer to the substrate and also its thermal stability as shown by thermal gravimetric analysis. In addition, the double or triple bond, which is strategically placed between the carboxylic acid group and the CF_2 groups, undergoes solid state polymerization when exposed to ultraviolet radiation or gamma rays. The polymerization results in a highly oriented thin polymer film which is insoluble due to cross-linking via the —C≡C— bond and consists of high molecular weight species. This film is conformal and pin-hole free. In addition, it has a low surface energy (contact angle of 94.5° with CH_2I_2). ESCA (Electron Spectroscopy Chemical Analysis) shows that the correct ratio of CF_3/CF_2 and C/F exists in the film. This film possesses the following advantages:

a. The deposition and polymerization occur at room temperature so that sensitive metallurgies are not subjected to thermal stresses.
b. The film thickness is molecularly engineered and controlled by the length of the extended chain monomer length.
c. The fluorocarbon groups are not subject to bacteria attack as are some fully hydrogenated fatty acids.
d. Also, by judiciously controlling the F/C ratio, the lateral cohesive energy between the molecules can be increased to improve upon the film's thermal stability.
e. Mechanical durability and thermal stability of a high molecular weight cross-linked polymer.

A long alkyl chain is required for the monomer used in the present invention. To compensate for the larger cross section diameter of the fluorocarbon segment, a long alkane chain is required to allow cross linking through the double or triple bond upon exposure to gamma rays or ultra violet radiation. This is a topotactic requirement for polymerization or cross-linking to occur. That is, the double or triple bond distance must be close enough to each other to form a sigma bond.

A certain fraction of conventional unsaturated compounds, for example omega-tridecenoic acid or alkenes, may be mixed in with the fluorinated monomer during monolayer formation in order to compensate for the larger cross-sectional diameter of the fluorinated group. The presence of such an unsaturated material contributes to the cross-linking.

The partially fluorinated fatty acids are synthesized by the procedures outlined and described below. These fatty acids are thereafter converted to metal salts thereof, each comprising a divalent cation.


$CF_3(CF_2)_nI + CH_2{=}CH{-}(CH_2)_m{-}OH$
AIBN/70—80°C
$CF_3(CF_2)_n{-}CH_2{-}CH(I){-}(CH_2)_m{-}OH$
Zn/HCl/EtOH
$CF_3(CF_2)_n{-}CH_2{-}CH_2{-}CH_2(CH_2)_m{-}OH$
$MsCl/(C_2H_5)_3N/Et_2O$
$CF_3(CF_2)_n{-}CH_2{-}CH_2{-}(CH_2)_m{-}OMs$
KI/Acetone
$CF_3(CF_2)_n{-}CH_2{-}CH_2{-}(CH_2)_m{-}I$
$HC \equiv C\ Li$
$Br(CH_2)_LCO_2C_2H_5$
n-Bu Li
$CF_3(CF_2)_nCH_2CH_2(CH_2)_m{-}C{\equiv}C{-}(CH_2)_LCO_2H$
5% Pd—$BaSO_4$
H_2
$CF_3(CF_2)_nCH_2CH_2(CH_2)_mCH{=}CH{-}(CH_2)_LCO_2H$
$CF_3(CF_2)_nI + CH_2{=}CH{-}(CH_2)_m{-}OH$
AIBN/70—80°C
$CF_3(CF_2)_n{-}CH_2{-}CH(I){-}(CH_2)_m{-}OH$
Zn/HCl/EtOH

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$CF_3(CF_2)_n—CH_2—CH_2—(CH_2)_m—OH$

↓ $MsCl/(C_2H_5)_3N/Et_2O$

$CF_3(CF_2)—CH_2—CH_2—(CH_2)_m—OMs$

↓ KI/Acetone

$CF_3(CF_2)_n—CH_2—CH_2—(CH_2)_m—I$

↓ Diisopropylamine; n-Bu Li; $HC \equiv C—\overset{\overset{O}{\|}}{C}OH$

$CF_3(CF_2)_n—CH_2—CH_2—(CH_2)_m—C \equiv C—\overset{\overset{O}{\|}}{C}OH$

↓ 5% $Pd—BaSO_4$; H_2

$CF_3(CF_2)_nCH_2CH_2(CH_2)_mCH=CH—\overset{\overset{O}{\|}}{C}OH$

Addition of 1-iodoperfluoroheptane to ω-undecylenyl alcohol using AIBN initiator. ω-undecylenyl alcohol (17.1 g.; 0.10 mole), 1-iodoperfluoroheptane (49.6 g.; 0.10 mole), and azobisisobutyronitrile (AIBN) (1.64 g.; 0.01 mole) were heated under nitrogen at 70—80°C for 5 hr. and cooled to room temperature, whereupon the whole mixture was solidified. Yield of the addition product was over 90%.

Zinc reduction of 1-iodoperfluoroheptane adduct to ω-undecylenyl alcohol — A solution of the addition product (0.10 mole) in 160 ml. ethyl alcohol was saturated with anhydrous hydrogen chloride and heated to 50—60°C. Zinc powder (9.8 g.; 0.15 mole) was added periodically at such a rate that no excessive foaming should occur. The solution was resaturated with dry hydrogen chloride at times when zinc dust failed to react. After the addition of zinc had been completed, the solution was continued to reflux for an hour. Alcohol was removed by distillation at reduced pressure and the residue was poured into water and extracted three times with ether. After drying over anhydrous magnesium sulfate, the solvent was removed under reduced pressure and the product, $CF_3CF_2)_6\ (CH_2)_{11}OH$ was isolated in 75% yield.

Anal. Calcd. for $C_{18}H_{23}F_{15}O$: C, 40.00; H, 4.26; F, 47.69

Found: C, 40.18; H, 5.10; F, 47.50

Reaction of $CF_3(CF_2)_6\ (CH_2)_{11}OH$ with methanesulfonyl chloride. To a solution of $CF_3(CF_2)_6\ (CH_2)_{11}OH$ (2.70 g.; 0.02 mole) in 50 ml. anhydrous diethyl ether was added 0.7 ml. of triethylamine and the solution was cooled to 0°C. Methanesulfonyl chloride (0.4 ml; 0.02 mole) was added dropwise. After stirring at 0°C for 0.5 hr., the reaction mixture was brought up to room temperature. The amine

hydrochloride salt was filtered off and the remaining ether solution was evaporated to dryness to give quantitative yield of $CF_3(CF_2)_6\,(CH_2)_{11}OMs$, m.p. 50°C.

Anal. Calcd. for $C_{18}H_{25}F_{15}O_3O$: C, 36.89; H, 4.05; F, 46.12

Found: C, 37.56; H, 4.12; F, 46.72.

Reaction of $CF_3(CF_2)_6\,(CH_2)_{11}OMs$ with Potassium Iodide — $CF_3(CF_2)_6\,(CH_2)_{11}OMs$ (6.68 g.; 0.01 mole) and potassium iodide (3.32 g.; 0.01 mole) in 200 ml. reagent acetone was heated to reflux for 2 hr., cooled to room temperature and the solid residue was removed by filtration. The remaining acetone solution was evaporated to dryness to give $CF_3(CF_2)_6\,(CH_2)_{11}I$ in 85% yield, m.p. 32°C.

Anal. Calcd. for $C_{18}H_{22}F_{15}I$: C, 32.23; H, 3.38; F, 43.84

Found: C, 32.00; H, 3.35; F, 43.89.

Preparation of $CF_3(CF_2)_6\,(CH_2)_{11}$

$$C{\equiv}C{-}\overset{\overset{\displaystyle O}{\|}}{C}OH{-}$$

In a three-necked round bottom flask fitted with condenser, nitrogen inlet, drying tube, and septum were placed diisopropylamine (1.08 g. 0.01 mole), 21.0 ml. potassium-dry tetrahydrofuran and 3.0 ml. of hexamethylphosphoramide. The reaction mixture was cooled to −78°C in a dry ice-acetone bath. n-Butyllithium (4.5 ml. of 2.5 *M*; 0.01 mole) was added dropwise with a syringe. After stirring at −78°C for an hour, a 10% solution of propiolic acid (0.35 g.; 0.0005 mole) in hexamethylphosphoramide (3.5 g.) was added dropwise while keeping the temperature below −60°C. After stirring at −78°C for an hour $CF_3(CF_2)_6\,(CH_2)_{11}I$ (3.03 g.; 0.005 mole) in tetrahydrofuran (35 ml.) and hexamethylphosphoramide (5 ml.) was added dropwise. After an additional two hours, the reaction mixture was brought to room temperature, and let stir for 2 hours before hydrolysised with water. Acidification of the solution with dilute HCl was followed by extraction three times with diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulfate.

$$CF_3(CF_2)_6\,(CH_2)_{11}C{\equiv}C{-}\overset{\overset{\displaystyle O}{\|}}{C}OH$$

was isolated in 60% yield after all of the solvent had been removed under reduced pressure, m.p. 70°C.

Anal. Calcd. for $C_{21}H_{23}F_{15}O_2$: C, 42.57; H, 3.88; F, 48.14

Found: C, 42.50; H, 3.98; F, 48.10

The monolayers were prepared from a 1×10^{-3} molar solution in chloroform. Approximately 100 μl of solution were placed on the water surface, drop by drop. The water was buffered to a pH from 6 to 7 and a temperature of 19 to 20°C. A weight of 70 mg (27 dynes/cm) pulled the float, compressing the monolayer coverage to an area of approximately 6.3 × 30 cm. Transfer to fused silica substrates was accomplished by dipping into and out of the tank.

Non-polymerized salt of partially fluorinated fatty acid comprising a divalent cation gave a contact angle of 94.5° with methylene iodide, showing a low energy surface. Cross linking was accomplished with a uv lamp and was monitored by the disappearance of the unsaturation.

These unsaturated polymerized salts of partially fluorinated fatty acids convert a high energy surface to a low energy surface giving better lubricating properties. The layer of polymerized salt of fatty acid showed improved adhesion to the substrate as well as the low surface energy.

Claims

1. A method of forming a layer of polymer on a substrate surface comprising depositing on the substrate surface a monomolecular layer of a monomer, characterised in that the monomer has the formula

$$(CF_3{-}(CF_2)_n{-}(CH_2)_m{-}X{-}COO)_2\ M$$

or

$$(CF_3\text{—}(CF_2)_n\text{—}(CH_2)_m\text{—}X\text{—}(CH_2)_L\text{—}COO)_2\ M$$

wherein n is 6 to 20, each of m and L is 6 to 10, X is —CH=CH— or —C≡C—, and M is a divalent cation, and polymerizing said layer.

2. A method as claimed in claim 1, in which the polymerization is carried out by exposing the monomolecular layer to ultra violet or gamma ray radiation.

3. A method as claimed in claim 1 or 2, in which the substrate has a hydrophilic surface.

4. A method as claimed in claim 1 or 2, in which the substrate is made of metal oxide.

5. A method as claimed in claim 1 or 2, in which the substrate is made of silicon dioxide.

Revendications

1. Procédé de formation d'une couche de polymère sur la surface d'un substrat, comprenant de dépôt sur la surface du substrat d'une couche monomoléculaire d'un monomère, caractérisé en ce que le monomère a comme formule:

$$(CF_3\text{—}(CF_2)_n\text{—}(CH_2)_m\text{—}X\text{—}COO)_2\ M$$

ou

$$(CF_3\text{—}(CF_2)_n\text{—}(CH_2)_m\text{—}X\text{—}(CH_2)_L\text{—}COO)_2\ M$$

où n a une valeur comprise entre 6 et 20, bornes inclues, m et L ont chacun une valeur comprise entre 6 et 10, bornes inclues, X représente —CH=CH— or —C≡C—, et où M est un cation bivalent, et en ce que ladite couche est polymérisée.

2. Procédé selon la revendication 1, caractérisé en ce que la polymérisation se fait en exposant la couche monomoléculaire à des rayons gamma ou ultraviolets.

3. Procédé selon l'une des revendications 1 ou 2, caractérisé en ce que le substrat a une surface hydrophile.

4. Procédé selon l'une des revendications 1 ou 2, caractérisé en ce que le substrat est un oxyde de métal.

5. Procédé selon l'une des revendications 1 ou 2 caractérisé en ce que le substrat est du bioxyde de silicium.

Patentansprüche

1. Verfahren zur Herstellung einer Polymerschicht auf der Oberfläche einer Unterlage, bei dem auf der Oberfläche der Unterlage eine monomolekulare Schicht eines Monomeren abgeschieden wird, dadurch gekennzeichnet, daß das Monomere die Formeln

$$(CF_3\text{—}(CF_2)_n\text{—}(CH_2)_m\text{—}X\text{—}COO)_2\ M$$

oder

$$(CF_3\text{—}(CF_2)_n\text{—}(CH_2)_m\text{—}X\text{—}(CH_2)_L\text{—}COO)_2\ M$$

aufweist, in denen n 6 bis 20 und m und L je 6 bis 10 bedeuten; X bedeutet —CH=CH— oder —C≡C— und M ein divalentes Kation; und daß diese Schicht polymerisiert wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Polymerisation der monomolekularen Schicht durch Bestrahlen mit ultravioletter oder γ-Strahlung durchgeführt wird.

3. Verfahren nach den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß die Unterlage eine hydrophile Oberfläche aufweist.

4. Verfahren nach den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß die Unterlags aus einem Metalloxid besteht.

5. Verfahren nach den Ansprüchen 1 oder 2, dadurch gekennzeichnet, dass die Unterlag aus Silicium-dioxid besteht.